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CITATION:

Minomura, Shigeru. Polymerization of lower polyoxymethylene glycols under pressure. The Review of Physical Chemistry of Japan 1954, 23(2): 49-53

ISSUE DATE:

1954-02-15

URL:

<http://hdl.handle.net/2433/46696>

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POLYMERIZATION OF LOWER POLYOXYMETHYLENE GLYCOLS UNDER PRESSURE

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Introduction

It has been already reported by the author and his co-workers^{1,2)} that the chemical equilibrium in the solid or liquidal reaction, such as the cis-trans isomerization of maleic acid, the intramolecular rearrangement of β -phenylhydroxylamine, or the coagulation of egg albumin, shifts to the production of the form of smaller molecular volume with increasing pressure. Besides, it has been also experimented that the dehydration of the solid material, such as ammonium bicarbonate, calcium sulphate, or pinacol, can be caused by the shearing stress between the molecules under ultra high pressure at room temperature. Now, the effect of pressure on the conversion of lower polyoxymethylene glycols to higher homologs was measured in order to confirm the above consideration. According to Staudinger³⁾, the acetone-soluble lower polyoxymethylene glycols gradually lose water on standing over phosphorus pentoxide, with a resulting increase in formaldehyde content and the polymers become completely insoluble in hot acetone. The author obtained two kinds of lower polyoxymethylene glycols in a fair degree of chemical purity and measured the effect of pressures (1 ~ 7500 atm) on the formaldehyde content of the solid polymeric glycols at room temperature (about 10° C) and elevated temperatures (80° C and 120° C).

Experimentals

Material Lower polyoxymethylene glycols consist of 2~8 formaldehyde units and 1 combined water per molecule, as shown by $\text{HO} \cdot (\text{CH}_2\text{O})_{n-1} \cdot \text{H}$. They differ from paraformaldehyde and other higher homologs in being soluble in acetone and ether, dissolving with little or no decomposition. Their solubilities in acetone decrease with increasing formaldehyde content per molecule. They dissolve rapidly in warm water with hydrolysis and depolymerization to form a formaldehyde solution. They are insoluble in petroleum ether.

According to the method of Staudinger⁴⁾ and the above described physical proper-

1) R. Kiyama and S. Minomura, *This Journal*, 22, 4, 9, 43 (1952), 23, 38 (1953)

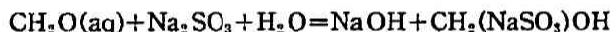
2) R. Kiyama and T. Yanagimoto, *ibid.*, 21, 32, 41 (1951), 22, 34, 39 (1952)

3) H. Staudinger, R. Signer, H. Johner, M. Lüthy, W. Kern, D. Russidis and O. Schweitzer, *Ann. Chem.*, 474, 255 (1929)

4) H. Staudinger, *Die Hochmolekularen Organischen Verbindungen* p. 248, Berlin, Julius Springer (1932)

ties, the following procedure was performed to obtain the lower polyoxymethylene glycols with a certain average degree of polymerization. Commercial paraformaldehyde was dissolved in distilled water by boiling (approximately 50 % aqueous formaldehyde solution) and the insoluble substance was separated by filtering. The filtrate was concentrated below atmospheric pressure in the water-bath at about 50° C until the solution became viscous liquid. It was dissolved by a certain amount of acetone in a flask with a reflux condensor and the hot acetone solution was filtered. When the filtrate was allowed to stand at about 35° C for 2 days, the wax-like solid was precipitated. The filter residue was used as sample A. The lower polyoxymethylene glycols in the filtrate were obtained by fractional precipitation with petroleum ether and the filter residue was used as sample B. Samples A and B were air-dried at room temperature for 4 weeks. Then sample A was dried over quicklime in a desiccator. Sample B was only air-dried. After it was ascertained that the per cent formaldehyde of the samples under the above conditions did not change in the lapse of days, the samples were used for the following experiment. Sample A had 93.0 % formaldehyde content (average 8.0 formaldehyde units per molecule) and melted at 115° ~ 120° C with decomposition. Sample B had 90.3% formaldehyde content (average 5.6 formaldehyde units per molecule) and melted at 105° ~ 110° C with decomposition.

Quantitative analysis of solid formaldehyde polymers The sodium sulfite method⁵⁾ was used to determine formaldehyde, because of its accuracy, simplicity and rapidity. The method is based on the quantitative liberation of sodium hydroxide, when formaldehyde reacts with sodium sulfite according to the following equation :



About 150 mg of formaldehyde polymers was weighed in a weighing bottle, placed with distilled water in a 250 cc volumetric flask, stopped tightly with a stopcock, warmed in a water-bath at about 65° C for 12 hours, dissolved completely, cooled and diluted exactly to a 250 cc aqueous solution. Besides, about 40 cc of 0.2 N aqueous solution of sodium sulfite and a drop of thymolphthalein indicator solution (0.1 % in alcohol) were placed in a 150 cc Erlenmeyer flask and carefully neutralized by 0.1 N sulfuric acid until the blue color of the indicator disappeared. 50 cc aliquot of the aqueous formaldehyde solution was added to the neutralized sodium sulfite and the resulting mixture was titrated with 0.1 N standard sulfuric acid to complete decoloration. 1 cc of normal acid is equivalent to 0.03002 g formaldehyde and the per cent formaldehyde (F) in the sample is determined by the equation :

$$F = \frac{\text{acid titer} \times \text{normality of acid} \times 3.002}{\text{weight of sample}}$$

The analytical figures obtained for the solid formaldehyde polymers by the sodium

5) J. F. Walker, *Formaldehyde*, p. 257, New York, Reinhold Publishing Corp. (1944)

sulfite method were accurate within approximately $\pm 0.05\%$. The average degree of polymerization (P) of the formaldehyde polymeric glycols was calculated by the equation:

$$P = \frac{18.01 F}{30.02 (100 - F)}$$

Procedure The average per cent formaldehyde of samples A and B preserved for certain hours (0 ~ 4 hours) under various pressures (1 ~ 7500 atm) at room temperature (about 10°C) and elevated temperatures (80°C and 120°C) was measured. The experimental procedures by a glass sealed tube and a high pressure apparatus were the same as the previous reports¹⁾. After the reaction, sample A was dried over quicklime in a desiccator for 2 days and sample B was air-dried for 5 days. At the same time it was also checked that the formaldehyde content of both original samples did not change by the drying under the above each condition.

Experimental result

The formaldehyde content of samples A and B at room temperature (about 10°C) did not change until 10,000 atm. The variation of the per cent formaldehyde and the average degree of polymerization of samples A and B preserved for various hours in a glass sealed tube and under 5000 atm at 80°C and 120°C are plotted against time in Fig. 1. The per cent formaldehyde in a glass sealed tube and under 5000 atm seems to approach equilibrium for 4 hours. The values of both samples for 4 hours at 120°C are about 1% higher than those for 4 hours at 80°C under the same pressure respectively. The values of both samples for 4 hours under 5000 atm are about 1.5% higher than those for 4 hours in the glass sealed tube at each elevated temperature respectively.

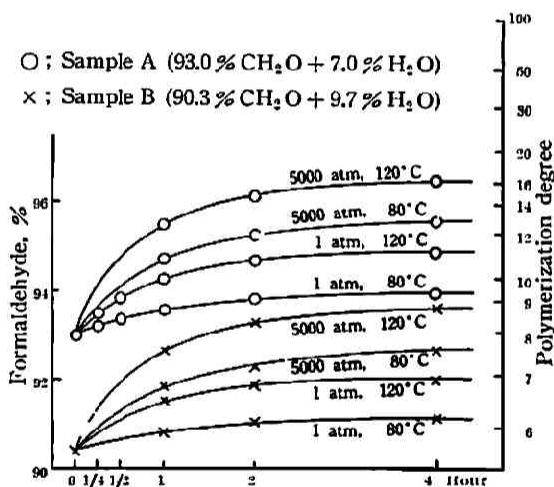


Fig. 1

The variation of the per cent formaldehyde and the average degree of polymerization of samples A and B preserved for 2 hours under various pressures at 80°C and 120°C are plotted against pressure in Fig. 2. The per cent formaldehyde increases in the same slope with increasing pressure at each temperature. The values of both samples under 7500 atm are about 2.3% higher than those in the glass sealed tube at each elevated temperature respectively.

The conversion of the lower polyoxymethylene glycols to higher homologs under pressure at elevated temperature was demonstrated not only by the increase of the

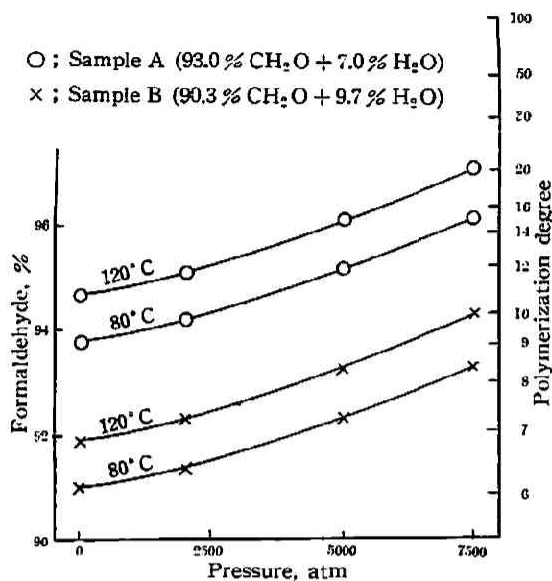


Fig. 2

formaldehyde content, but also by the decrease of the solubility in acetone. Sample A and the sample in the glass sealed tube were completely soluble in hot acetone at 55°C, but the insoluble polymeric glycols in the hot acetone in the samples under pressures, indicating the appearance of molecules containing 12 or less formaldehyde units⁴⁾, increased with increasing pressure at each elevated temperature. Similarly, sample B was completely soluble in warm acetone at 35°C, but the insoluble polymeric glycols in the warm acetone in the samples under pressures, indicating the appearance of molecules contain-

ing 8 or less formaldehyde units, increased with increasing pressure at each elevated temperature. As the compressed lower polyoxymethylene glycols were not hardened at room or elevated temperature and their appearance was wax-like solid, the decrease of the solubility of both samples in acetone was not owing to the mere consolidation of the samples by pressure, but to the increase of the average degree of polymerization.

The formation of cyclic polymers (trioxane and tetraoxymethylene) was not detected by extracting with acetone from about 2 g of sample A preserved for 2 hours under 5000 atm at 120°C.

Summary

The experimental results described above can be summarized as follows :

- (1) The formaldehyde content of lower polyoxymethylene glycols did not change at room temperature until 10,000 atm.
- (2) The formaldehyde content of lower polyoxymethylene glycols increased with increasing temperature, pressure and reaction time.
- (3) Every variation curve of the per cent formaldehyde of both samples at each elevated temperature for 2 hours against pressure had the same type of slope.
- (4) The solubility of both samples in acetone decreased with increasing pressure at each elevated temperature.

It may be concluded that the conversion of lower polyoxymethylene glycols to higher homologs is not caused at room temperature until 10,000 atm and the dehydration between glycol molecules increases with increasing pressure at elevated temperatures.

The author has great pleasure in expressing his sincere thanks to Prof. R. Kiyama for his valuable guidance during the course of this research. He is indebted to the Department of Education for the Grant to the Cooperative Research (The Fundamental Research on High Pressure Industries directed by Prof. R. Kiyama).

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